TECHNICAL MEMORANDUM

TO: Solomon Ricks / OAQPS

FROM: Eric Boswell / NAREL

AUTHOR: Steve Taylor / NAREL

DATE: September 20, 2005

SUBJECT: Performance Evaluation of R&P 8400 and Sunset Labs Ambient Air Monitors

Introduction

A Performance Evaluation (PE) study has been completed for semi-continuous nitrate, sulfate, and carbon ambient air monitors. Five sites located in different states continue to operate at least one of the 8400 series ambient air monitors manufactured by R&P. The 8400N and the 8400S units are designed to capture $PM_{2.5}$ from the ambient air and provide measurements of nitrate and sulfate respectively, every ten minutes. A new ambient air monitor manufactured by Sunset Laboratory Inc. has been installed recently at three different field sites located in or near Phoenix, AZ; Chicago, IL; and Seattle, WA. The Sunset monitor is a semi-continuous field instrument designed to collect fine particulate matter ($PM_{2.5}$) from the ambient air and then analyze the captured material for the presence of elemental carbon (EC) and organic carbon (OC). The new Sunset monitors have been programmed to automatically provide EC and OC measurements every hour. The sample collection time has been set at forty-seven minutes which leaves thirteen minutes to perform the sample analysis and get ready for the next sample collection. This is the fifth PE study of the R&P analyzers and the second PE study of Sunset's semi-continuous carbon analyzer.

Summary - R&P Semi-Continuous Nitrate and Sulfate Analyzers

Aqueous spike solutions have been used again to evaluate performance of the R&P semi-continuous nitrate and sulfate monitors. Five blind spikes covering a wide range of concentrations were analyzed in triplicate by each instrument. All of the sites were given identical sets of test solutions and/or filter samples depending on instrumentation at the site. The operators of the R&P analyzers were instructed to analyze the local blank water and the local calibration standard along with the test solutions.

Data comparisons between the filter based nitrate results and the R&P semi-continuous nitrate results have indicated a non-linear response at some of the sites. In a previous PE study, the R&P 8400N operators were asked to analyze a set of four nitrate spike solutions in addition to the five blind spikes. The extra solutions were prepared using ammonium nitrate, calcium nitrate, potassium nitrate, and sodium nitrate. These solutions were included to test the instrument's response to different forms of nitrate that may occur in ambient air. The PE analysis results of the individual salt solutions indicated that instrument response was virtually the same for each of the salts. In order to further examine the effects of various nitrate compounds on instrument response, one of the five nitrate PE solutions for this study was made from a mixture of four different nitrate salts with a sulfate component added.

The blind spike solutions of nitrate and sulfate were evaluated by preparing scatter plots for each monitor showing the mass of analyte reported versus the mass of analyte spiked into the instrument. A linear response and good precision was evident for most of the monitors. The special nitrate PE mixture consistently demonstrated a reduced recovery compared to the single salt solutions and was not included in calculating the regression. To further examine the data generated from the blind spike solutions, a linear calibration curve based upon analysis of the PE solutions themselves (excluding the nitrate mixture) was generated for each instrument, and new results were calculated. Based upon the new results from the calibration curves, all sites report about the same value for each PE solution, and good accuracy can be achieved over a wide calibration range for aqueous spikes. It is worth stating that an aqueous spike is not a captured ambient air deposit. However, the aqueous spike may be the most valuable single method to evaluate instrument performance, and it provides a basis for adjusting the raw data output from the pulse analyzer.

Summary - Sunset Semi-Continuous Carbon Analyzer

Replicate performance evaluation (PE) samples were prepared at EPA's National Air and Radiation Environmental Laboratory (NAREL) such that each site was given the same set of three PE samples with instructions to analyze each sample twice. One sample was blank, one sample was a sucrose spike, and one sample was loaded with $PM_{2.5}$ collected from the ambient air at NAREL. None of the site operators were given information about the PE samples beyond the sample tracking number. Analytical results were submitted to NAREL along with the raw data files.

Results from this study were evaluated by making two comparisons: (1) how well do results from all three sites agree since replicates were analyzed at all of the sites, and (2) how do the reported results compare to expected values? Both comparisons showed good agreement among the three sites and NAREL. The previous PE study discovered that the Arizona and Washington field sites were not using the most recent version of calculation software and that the accuracy of their expected results could be improved by recalculating their raw data files using the latest version of software. As a result of the first PE discovery, Sunset installed updated versions of the calculation software at the two sites. This study has found that slightly different versions of calculation software continue to be used at each site, however, the differences appear to be much less significant than found in the previous study. Although slightly different versions of the calculation software are being used, this study has shown that the Sunset instrument continues to give good performance at all three field sites.

Experimental Design - R&P Semi-Continuous Nitrate and Sulfate Analyzers

Blind aqueous spike solutions were prepared at the National Air and Radiation Environmental Laboratory (NAREL) located in Montgomery, AL. PE solutions were prepared from the same salts and chemicals that are present in the local calibration solutions used at each field site. Four of the five nitrate PE solutions were prepared using KNO_3 and 18 mega-ohm laboratory water which was passed through a 0.2-µm membrane filter immediately before use. Sulfate PE solutions were prepared by dissolving NH_4SO_4 and oxalic acid into the same laboratory water previously described. The oxalic acid was added to each sulfate solution at a rate of 4 mg of carbon (from the oxalic acid) per 3 mg of sulfate (from the NH_4SO_4). All PE solutions were analyzed using a Dionex DX500 Ion Chromatograph configured for the analysis of anions. All PE solutions were verified to be within 5 % of the nominal concentration of nitrate and sulfate before they were shipped to the site operator. The concentration of nitrate and sulfate present in each PE solution is listed in Table 3 and Table 5 respectively, at the end of this report.

One special nitrate solution, N3-05-05, was prepared using a mixture of four nitrate salts. Sulfate was also added to the PE mix using $(NH_4)_2SO_4$. The final solution was composed of 250 ppm NO_3^- from NH_4NO_3, 50 ppm NO_3^- from $Ca(NO3)_2$, 50 ppm NO_3^- from KNO_3, 50 ppm NO_3^- from $NaNO_3$, and 400 ppm SO_4^- from $(NH_4)_2SO_4$. The final concentration of the sample was 400 ng/µL NO_3^- with 400 ng/µL SO_4^-.

A new syringe was provided to each site operator with instructions to use the new syringe for all spiking during this study. Normally each instrument is calibrated by injecting different volumes of one [local] spike solution to establish the calibration range. For this study five PE solutions were provided for each instrument to establish a calibration range using only one spike volume. The purpose for using only one spike volume was to keep the amount of water deposited onto the flash strip constant for all spikes. The new syringe was used to deliver one spike volume for all solutions described in this report.

The site operator was instructed to perform a manual audit of the pulse analyzer before starting the aqueous spikes. Audit results from the 8400N and the 8400S are presented in Table 3 and Table 5 respectively, at the end of this report.

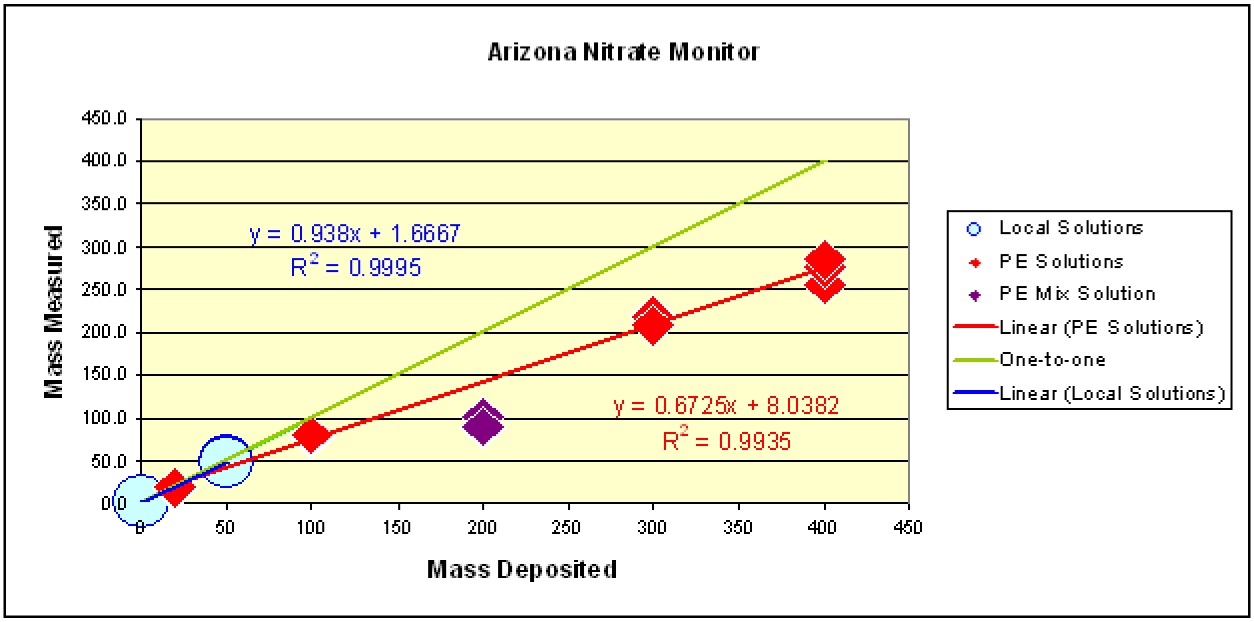
Analysis of the Blind Aqueous Nitrate Spike Solutions

Site operators were instructed to perform triplicate analysis of the aqueous solutions using only one spike volume, 0.5 µL. The analysis began with the local blank water followed by analysis of the local 100 ng/µL nitrate standard. The study continued by running the five *blind* solutions identified simply as N1-05-05 through N5-05-05. The results reported from the sites are included in Table 4 at the end of this report along with the previously undisclosed concentration of each PE solution. An extra column of "Re-calculated Results" has also been added to Table 4. Results from each site were re-calculated from a calibration curve based upon the four KNO_3 PE solutions analyzed at that site. By re-calculating all results from a calibration curve, the new results are corrected for inefficient pulse generation and analysis. This is our way of normalizing the data to, hopefully, achieve better agreement from all the sites.

Results from a single site are presented as a scatter plot in Figure 1 through Figure 5. The mass measured versus the mass deposited is plotted for each spike. Results from the KNO_3 PE solutions are colored red in the plots, and results from the local blank water and local 100 ng/µL solution are presented in blue.

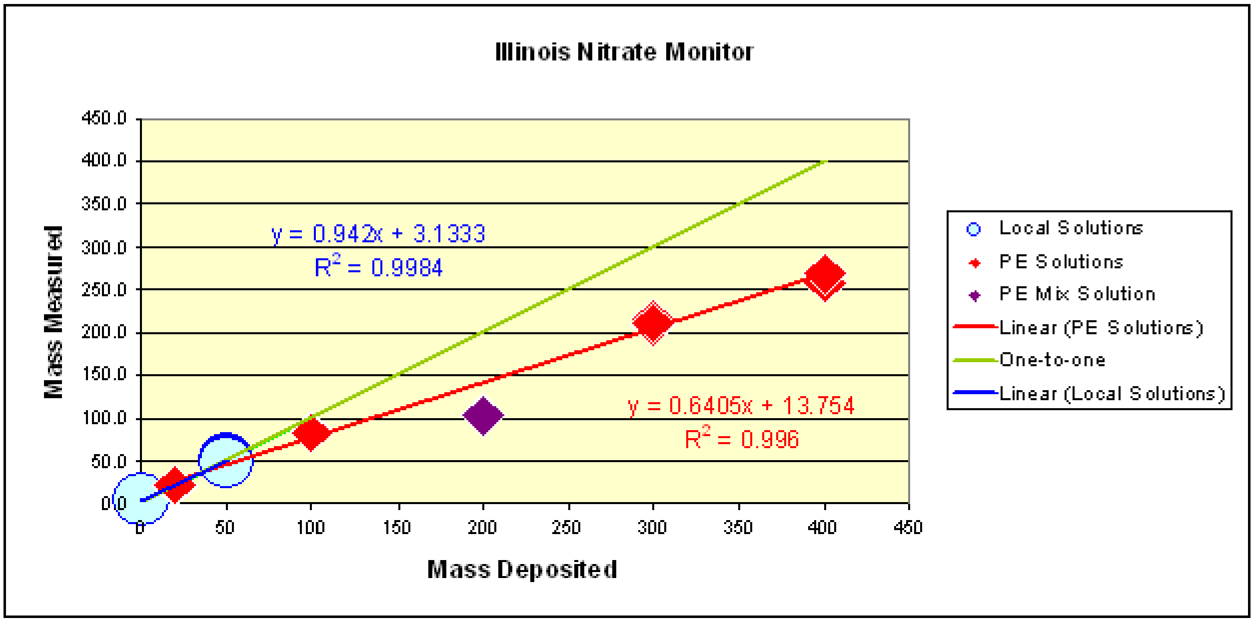
Results of the PE mixture solutions are presented in violet in the plots. Each plot also shows a green "One-to-One" line which represents perfect agreement between the mass measured and the mass deposited. The figures graphically illustrate a reduced instrument response for the PE mixture solutions compared to the single salt KNO_3 spike solutions.

Figure 1



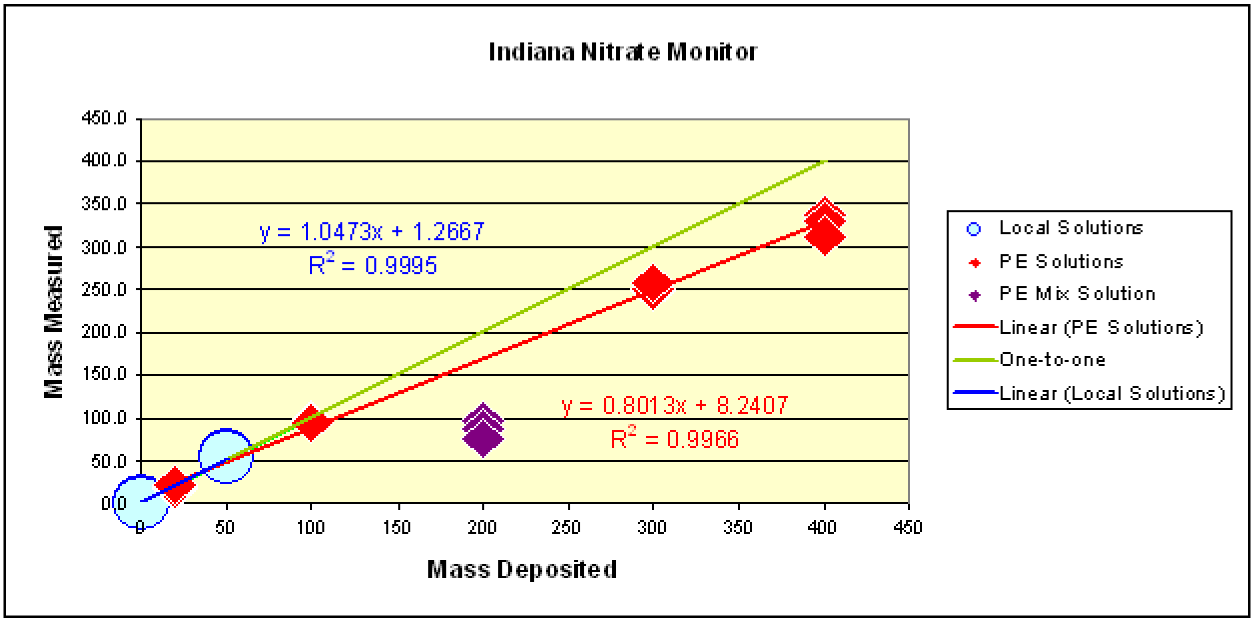
Good precision was observed for the nitrate spikes shown in Figure 1.

Figure 2



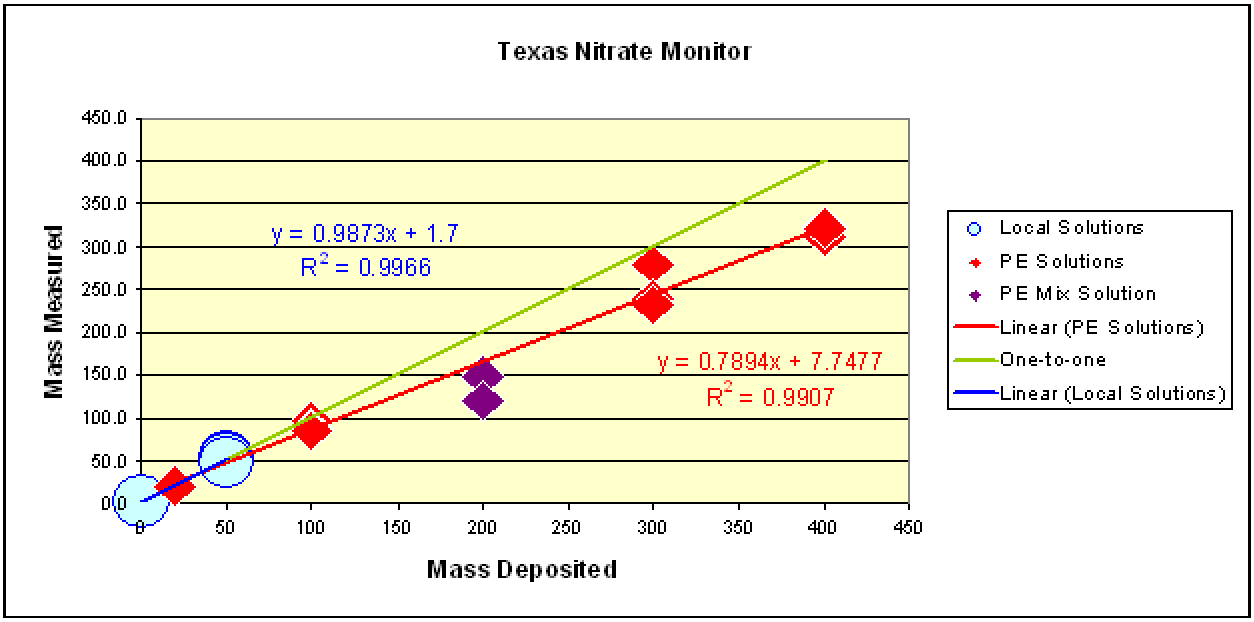
Excellent precision was observed for the nitrate spikes shown in Figure 2.

Figurer 3



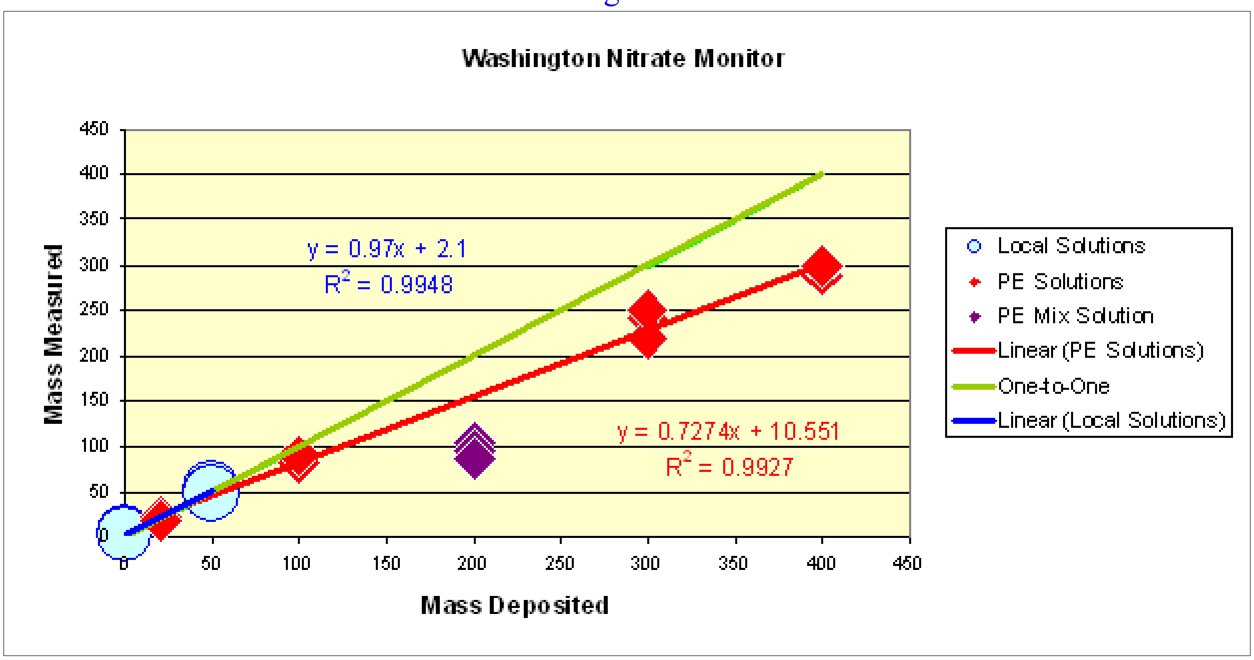
Good precision was also observed for the nitrate spikes shown in Figure 3.

Figure 4



Relatively good precision was observed for the nitrate spike solutions shown in Figure 4.

Figure 5



Good precision was observed for the nitrate spikes shown in Figure 5.

Figure 6

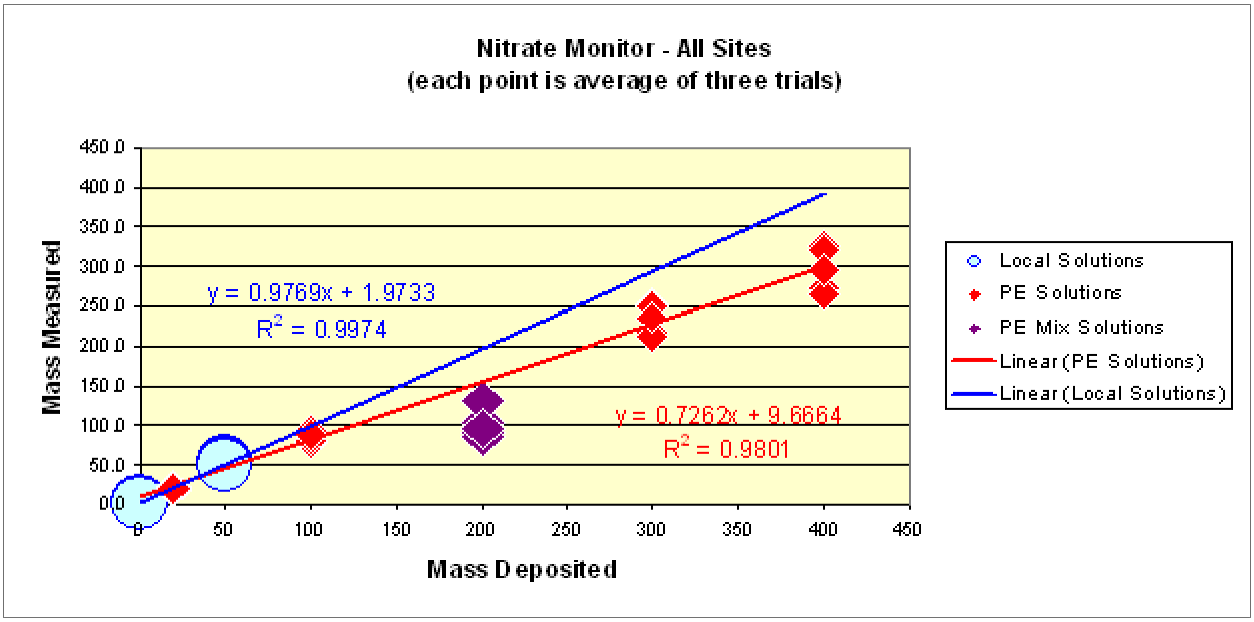


Figure 6 compares all results from all five sites. To simplify the graph, each point represents an average result from three replicate spikes of the same spike solution.

Figure 7

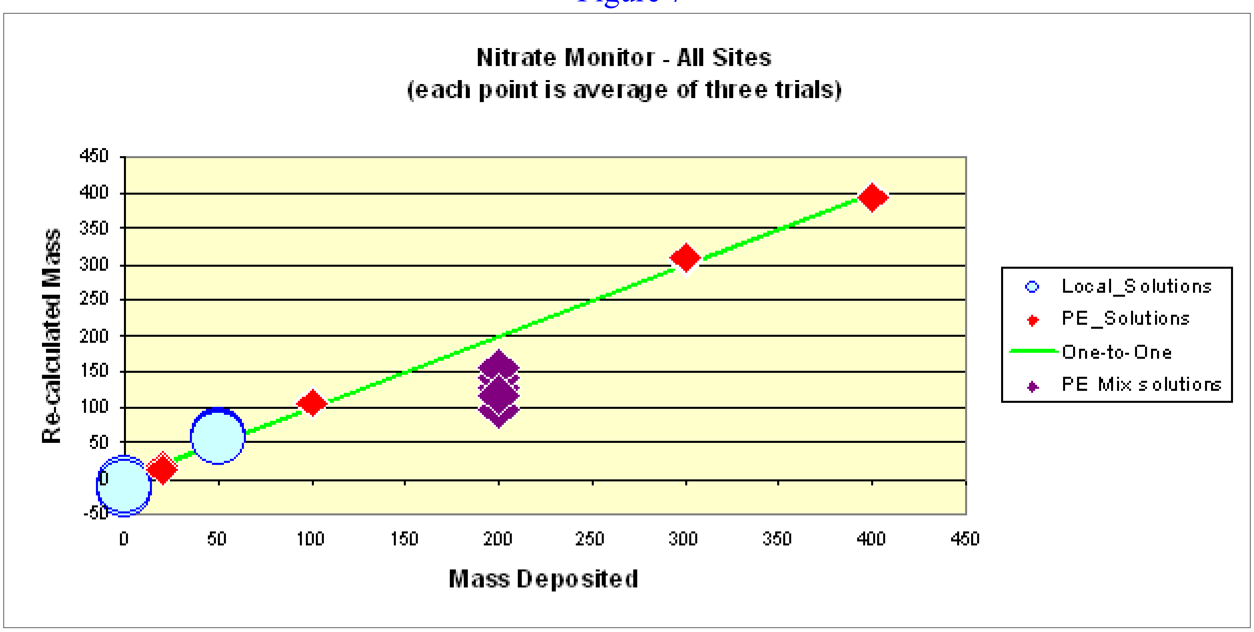


Figure 7 shows re-calculated mass from all of the sites. The results shown in Figure 7 were re-calculated from a calibration curve established at each instrument by analysis of the four KNO_3 PE solutions themselves. If the calibration curve at each instrument had been perfect, all of the re-calculated data points of the KNO_3 PE solutions shown in Figure 7 would fall exactly on the green One-to-One line. Again, the re-calculated masses of the PE mixture solutions consistently show a reduced response.

Analysis of the Blind Aqueous Sulfate Spike Solutions

Three of the five sites, Illinois, Texas, and Washington participated in the PE of the R&P 8400S sulfate monitor. Site operators were instructed to perform triplicate analysis of the aqueous solutions using only one spike volume, 0.5 µL. The analysis began with the local blank water followed by analysis of the local 300 ng/µL sulfate standard. The study continued by running the five *blind* solutions identified simply as S1-05-05 through S5-05-05. The results reported from the sites are included in Table 6 at the end of this report along with the previously undisclosed concentration of each PE solution. An extra column of "Re-calculated Results" has also been added to Table 6. Results from each site were re-calculated from a calibration curve based upon the PE solutions analyzed at that site. By re-calculating all results from a calibration curve, the new results are corrected for inefficient pulse generation and analysis. This is our way of normalizing the data to, hopefully, achieve better agreement from all the sites.

Results from a single site are presented as a scatter plot in Figure 8 through Figure 12. The mass measured versus the mass deposited is plotted for each spike. Results from the PE solutions are colored red in the plots, and results from the local blank water and local 300 ng/µL solution are presented in blue. Each plot also shows a green "One-to-One" line which represents perfect agreement between the mass measured and the mass deposited.

Figure 8

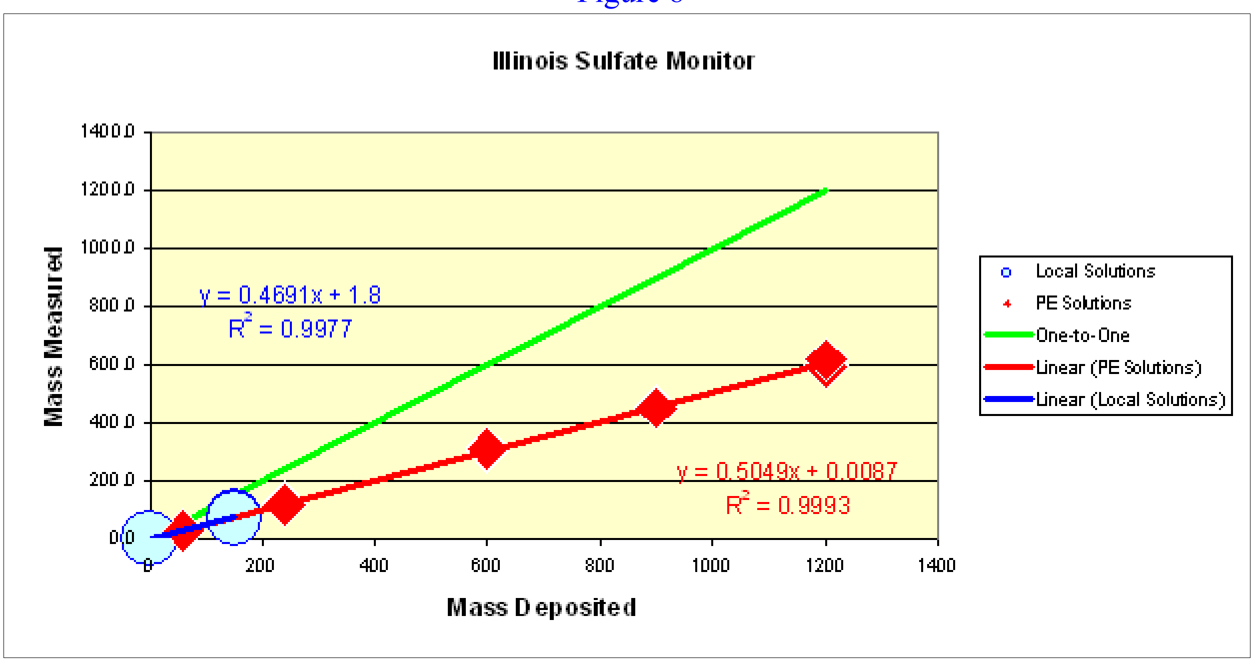


Figure 9

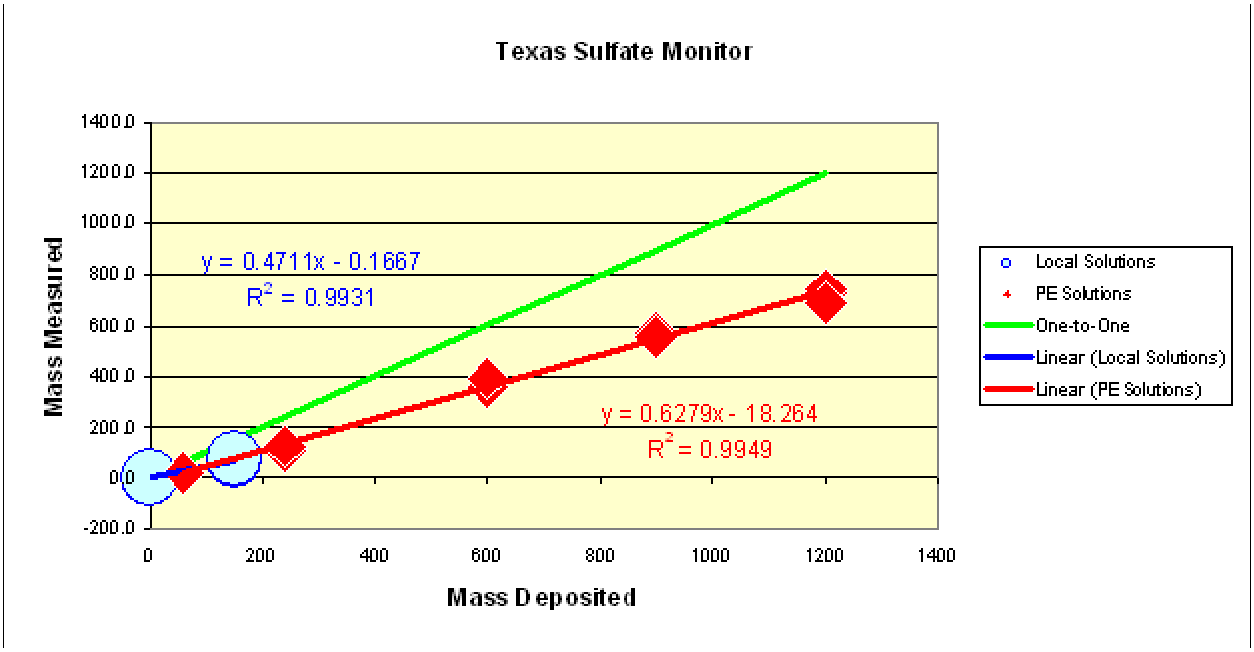


Figure 10

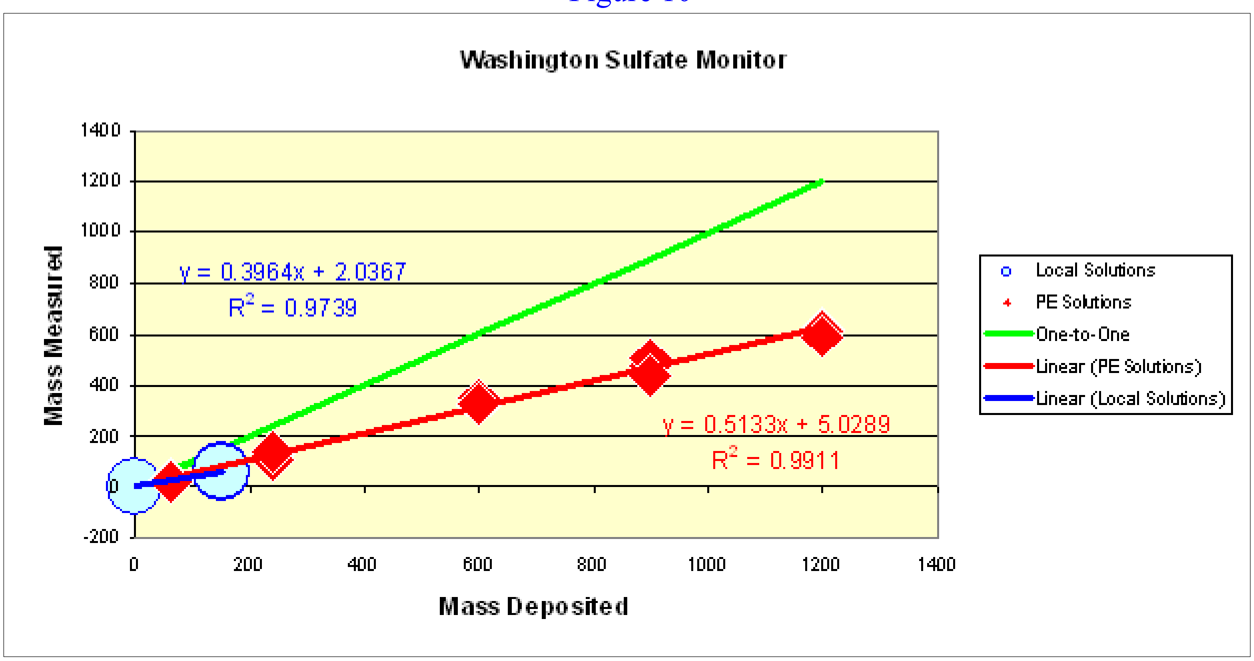


Figure 11

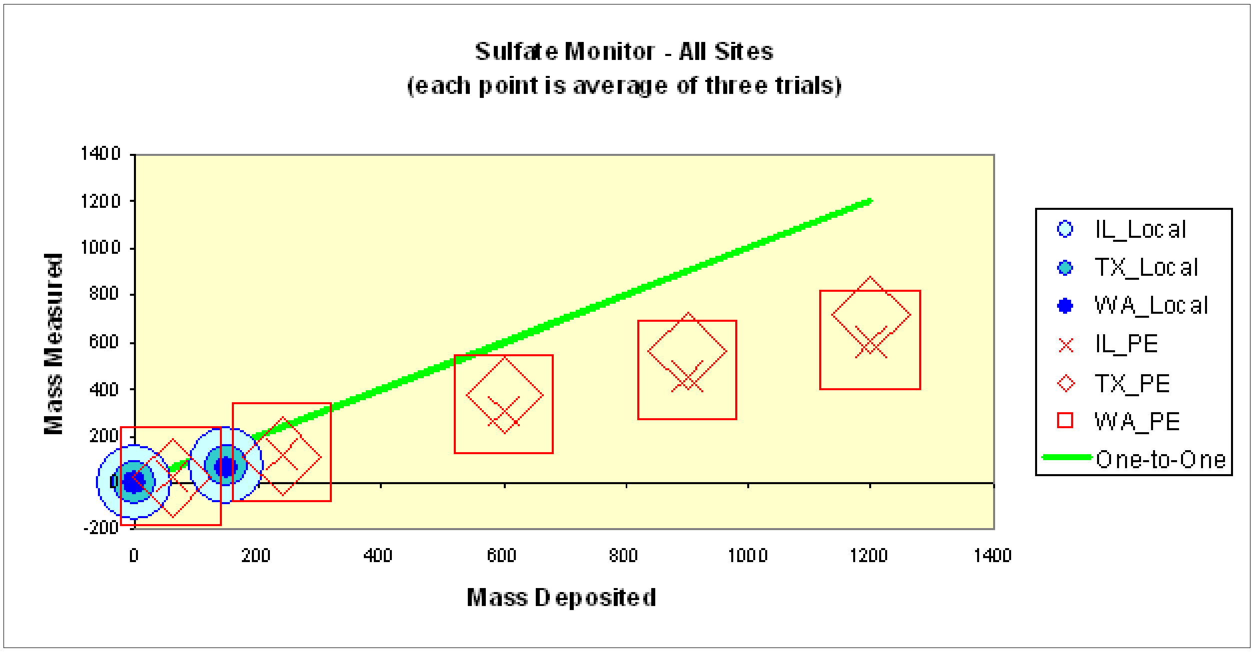
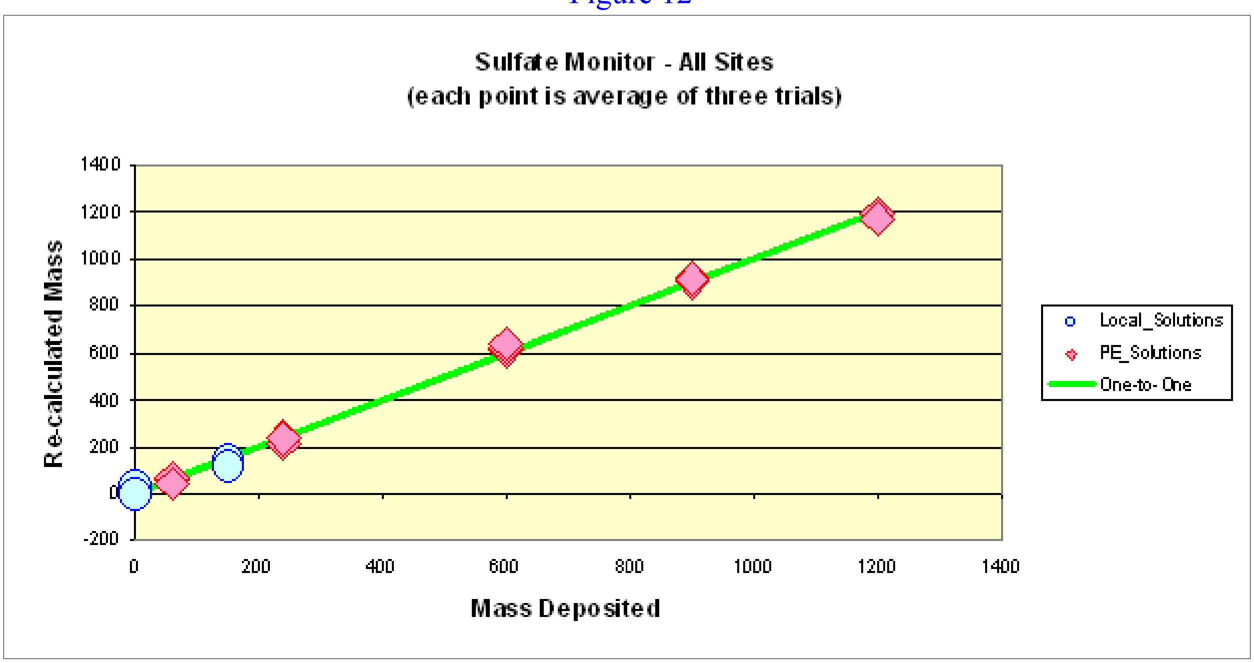


Figure 11 contains results from all three sites. To simplify the graph, each point represents an average result from three replicate spikes of the same spike solution. Each site is represented by a different symbol as shown in the plot legend.

Figure 12 shows re-calculated mass from all of the sites. Results were re-calculated from a calibration curve established at each instrument by the analysis of PE samples. Again, notice how well the re-calculated results in Figure 12 fit the green One-to-One line, but the uncorrected results in Figure 11 consistently fall below the One-to-One line.

Figure 12



Experimental Design - Sunset Semi-Continuous Carbon Analyzers

This study was designed to submit three types of samples to each field site: blanks, sucrose spikes, and ambient $PM_{2.5}$ (fine particles). Several replicates of each sample type were prepared at NAREL so that an identical set of samples was submitted to each site with instructions to analyze duplicates of each sample type. Four replicates of each sample type were actually provided to each site. The extra replicates were included within each set of samples to provide a means of recovery from an innocent accident such as dropping the sample onto the floor. The site operator could also use some of the extra replicates to practice procedure steps which were developed specifically for the PE studies.

All of the samples used in this study were prepared using a quartz fiber substrate which was purchased from Gelman as circular filters having a 47-mm diameter. A large batch of the new filters were cleaned by heating to 500 °C inside a muffled furnace for at least two hours after which the filters were placed into sealed Petri dishes and stored at freezer temperature until needed. Two of the filters in the batch were analyzed for EC and OC residues using a Sunset laboratory instrument set up to perform the Thermal Optical Transmittance (TOT) analytical method approved for the Speciation Trends Network (STN method). The STN method performed at NAREL is similar to the field method but includes some fundamental differences in the hardware and configuration. Results from the two test filters showed less than 0.2 $\mu gC/cm^2$ so the batch of filters was declared sufficiently clean for use.

Several of the clean 47-mm filters were assembled into canisters which were used to collect $PM_{2.5}$ from the Montgomery air. Co-located Super SASS units were programmed to load the filters with a lengthy 168-hour collection event. The long collection time was necessary to get the amount of collected EC high enough for the study. After the collection event was completed, the loaded filters were recovered from the canisters and placed individually into labeled Petri slides and stored at freezer temperature until needed. To gain confidence in the quality of filter replication, a small punched segment was removed from each loaded filters and analyzed using the STN method. Good precision was observed for the measured EC and OC with relative standard deviations at 7% and 3% respectively.

This study was designed to submit small circular punches of the quartz filter to the field sites so that each test sample could be installed into the instrument with minimum effort from the operator. Each circular punch must have a 16-mm diameter to fit properly into the instrument. A circular punch device was used to cut 16-mm circles from the larger 47-mm quartz filters. A large number of the 16-mm blank quartz circles were required for this study. Some of them were analyzed directly as a test sample. Some of them were spiked with an aqueous solution of sucrose. The sucrose spikes were allowed to air dry for about thirty minutes before they were packaged for shipment. Therefore it was not possible for the field operator to visually see a difference between the blank test samples and the test samples spiked with sucrose. Each field site was supplied with four Petri slides as described in Table 1.

Table 1. Components of the Sample Kit Submitted To Each Field Site		
Petri Slide Count	**Petri Label**	**Description of the Petri Slide Contents**
First	C1-05-05	Test sample replicates (four blank quartz circles)
Second	C2-05-05	Test sample replicates (four circles spiked with sucrose)
Third	C3-05-05	Test sample replicates (four circles loaded with $PM_{2.5}$)
Fourth	Blank quartz	twelve designated blank quartz circles **
***** each test sample must be mounted into the instrument with a designated blank circle***		

This study required the operator to temporarily interrupt the automated analysis of ambient air at his site, remove the collection filter from his instrument, and then use his instrument to analyze the test samples listed in Table 1. Table 1 shows that each site received twelve test samples and twelve designated blank circles. A designated blank circle was available for each test sample provided to the site. The operator was instructed to mount a designated blank circle into the instrument along with each test sample. This procedure was necessary to maintain normal behavior of the transmitted laser signal. The laser normally transmits through the collection filter. The collection filter, which was temporarily removed from the instrument, is actually two filters mounted together for extra strength. Since each PE sample will be a replacement for the collection filter, the PE sample should be doubly thick as well.

Analysis of the Carbon PE samples

Detailed instructions for analyzing the PE samples were provided to the site operators. As stated earlier, the normal automated analysis of ambient air was halted, and the collection filter was removed from the instrument. This study was designed to replace the collection filter with one of the test samples, and then run the instrument through the TOT analysis cycle. There was concern that results from the blank test samples might be high. High blank values can be caused by shipping and handling, but the greatest concern was for opening the instrument's oven each time a new test sample was installed. Because of this concern, the sucrose spike level was relatively high, and the $PM_{2.5}$ test sample was loaded with a relatively high level of OC.

Figure 13 shows the total carbon (TC) results for the sucrose spikes and the $PM_{2.5}$ test samples. TC is simply the sum of the EC and the OC for this study. The results are expressed as micrograms of carbon released from the test sample. Results determined at NAREL are shown along with the results reported from the three field sites. It is important to understand that the results reported for NAREL were determined using the STN analytical method since NAREL does not have a field instrument. Figure 13 also includes the sucrose spike level as well as the uncertainty of measurements performed at NAREL. The results from all three sites look relatively good and good duplicate precision was observed for all of the sites.

Figure 13

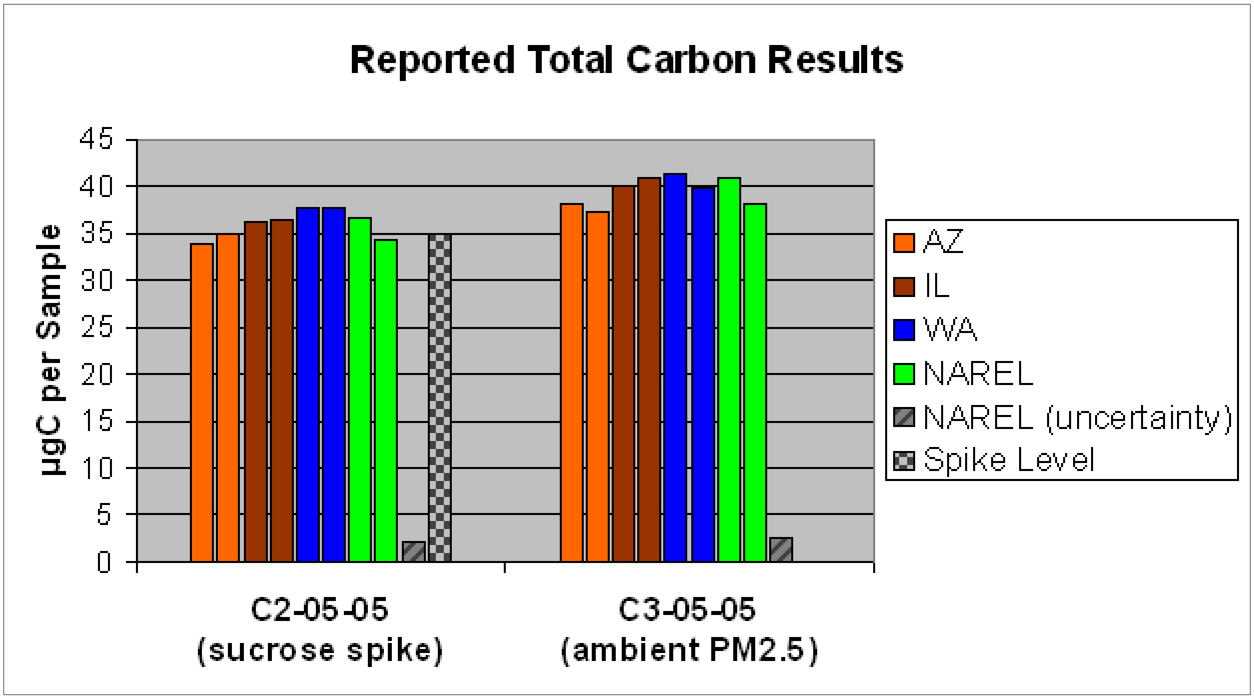


Figure 14

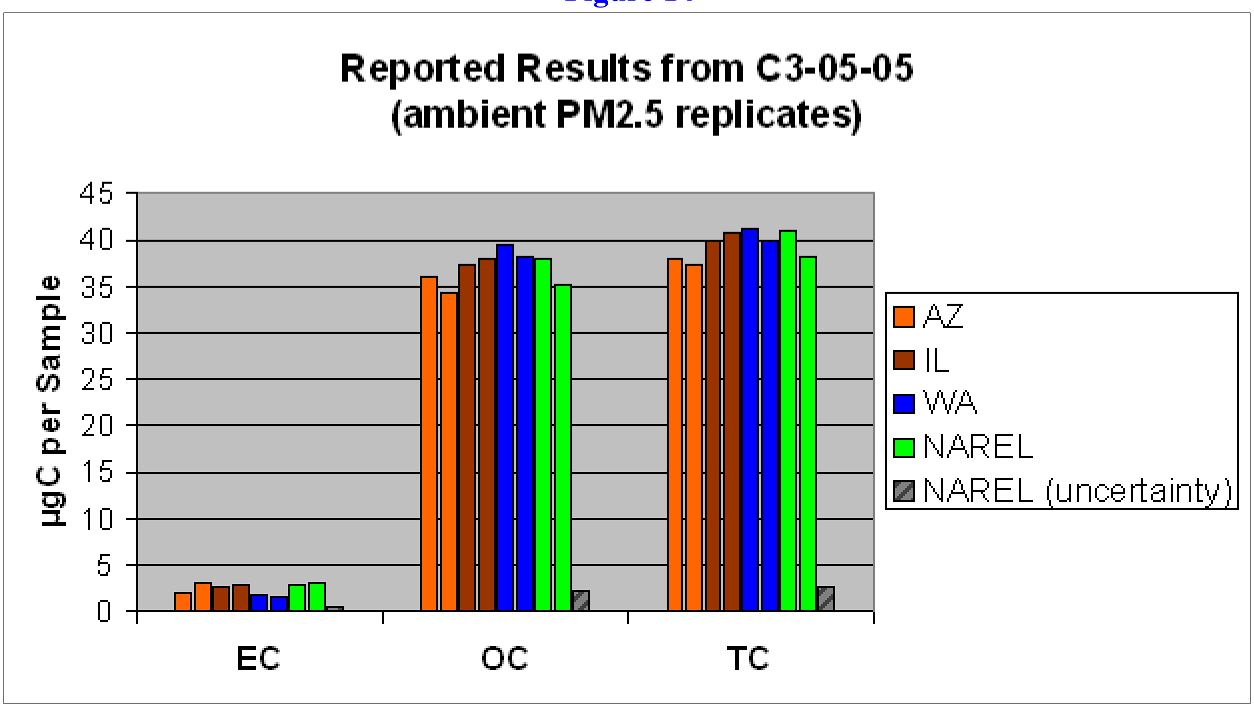


Figure 14 includes the EC and OC values along with the TC for the ambient $PM_{2.5}$ test sample. The sucrose spike sample is not presented in Figure 14 because sucrose does not contain EC and all of the sites correctly reported zero EC for the sucrose test sample.

All of the results reported from the sites and determined at NAREL are available in Table 7 at the end of this report. Results from the blank test circles were not presented in Figure 13 nor in Figure 14, but the blank results are included in Table 7.

During the first PE study of the Sunset, the raw data files along with the calculated result files were submitted to NAREL. After examining these files, it became clear that all of the sites were not using the same calculation software. NAREL recalculated results from the raw data files using a copy of the most recent calculation software (RTCCalc312.exe) provided by Sunset. The recalculated results from Washington showed significant improvement over the original results, and the recalculated results from Arizona showed some improvement. The recalculated results from Illinois were identical to the reported results, indicating that the Illinois site was using the most recent calculation software. Following the discovery of calculation software differences, Sunset Labs volunteered to install updated software at the Washington and Arizona sites. Raw data files for this study were again recalculated and compared to the results submitted by the field sites. Table 2 compares the the reported and recalculated TC results of C3, the $PM_{2.5}$ ambient air samples analyzed in both PE studies.

Table 2. Reported and Recalculated Total Carbon

		PE #1 Results (ug)			PE #2 Results (ug)		
Site	Sample*	Reported	Recalculated	RPD	Reported	Recalculated	RPD
Arizona	C3	24.05	28.15	15.7%	35.34	36.34	2.8%
	C3 dup	24.86	27.82	11.3%	38.05	40.45	6.1%
Illinois	C3	32.36	32.36	0.0%	39.95	39.95	0.0%
	C3 dup	32.76	32.76	0.0%	40.79	40.79	0.0%
Washington	C3	27.87	31.40	11.9%	41.29	41.33	0.1%
	C3 dup	26.63	31.44	16.6%	39.86	39.92	0.1%

* Ambient PM2.5 test sample

The recalculated results indicate that Washington and Arizona are not using the same version of calculation software as Illinois, however, a much smaller difference between reported and recalculated results was seen for this study.

Figures 15 and 16 graphically present the calculated and recalculated results for both the sucrose spike and the ambient air samples. All of the recalculated values including those presented in Figure 15 and Figure 16 are shown in Table 8 at the end of this report.

Figure 15

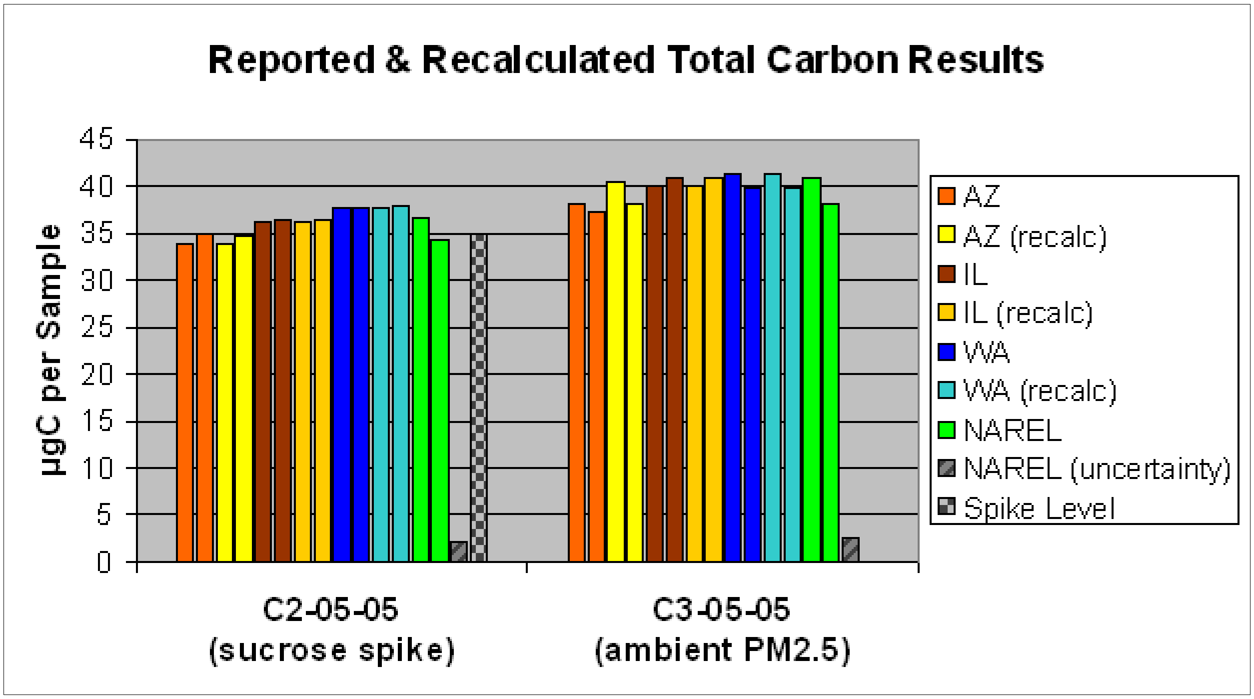
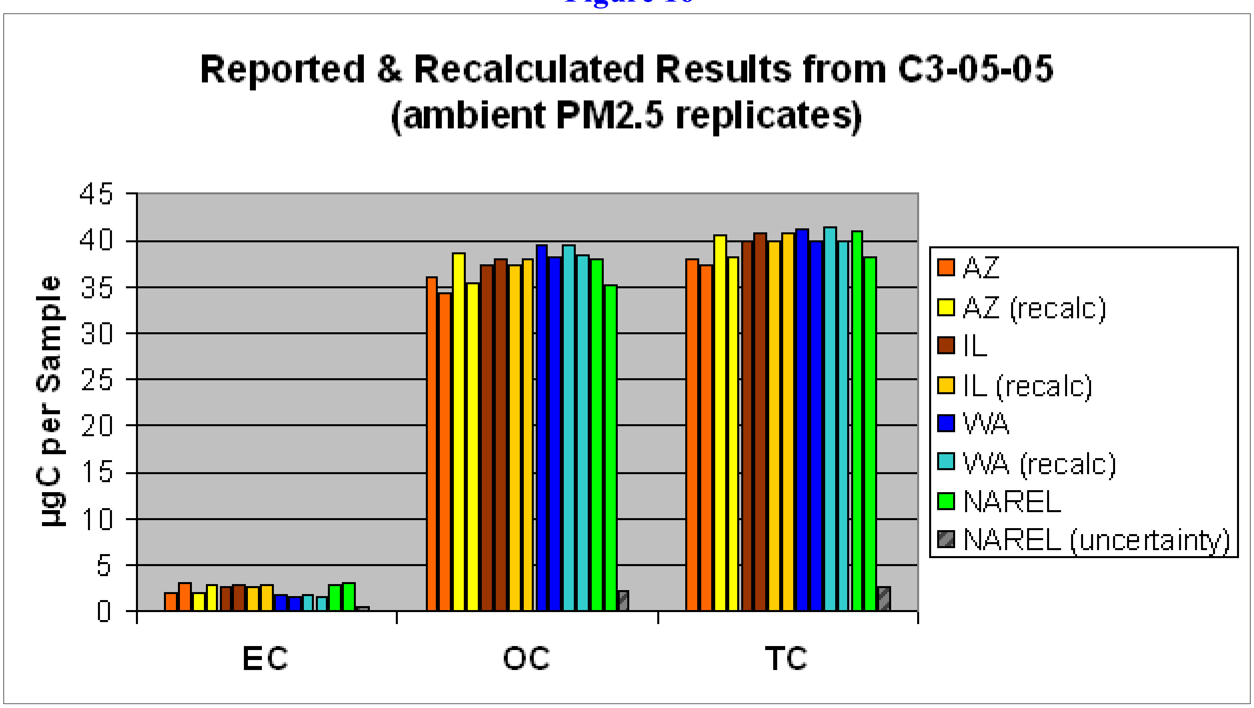


Figure 16



Conclusions

This PE study included both the R&P 8400 nitrate and sulfate analyzers as well as the Sunset Labs carbon analyzers. These monitors are designed to operate unattended at remote field sites to collect measurement data for nitrate, sulfate and carbon contained in ambient $PM_{2.5}$. This study was not designed to evaluate the overall performance of the monitors since the overall performance includes both sample collection and sample analysis. This study was designed, however, to evaluate the accuracy and precision of the sample analysis. This study, similar to previous studies, used single blind spike solutions to evaluate the R&P and Sunset analyzer performance. The Sunset analyzers were also able to analyze samples created by collecting replicate $PM_{2.5}$ samples on quartz filters.

As in previous studies, both the R&P nitrate and sulfate analyzers continued to show good precision and linear response for analysis of the blind spike solutions. Results from each site were recalculated from a calibration curve based upon the PE solutions analyzed at that site in order to normalize the data. By recalculating all results from a calibration curve, the new results are corrected for inefficient pulse generation and analysis. The normalized data indicates that all sites report about the same value for each PE solution, and good accuracy can be achieved over a wide calibration range for aqueous spikes.

One of the five nitrate PE solutions was made using a mixture of four different nitrate compounds instead of the single salt KNO3 solution normally used for the routine calibration of the R&P 8400N nitrate analyzer. Analysis results of the nitrate PE spike solutions presented in Figures 1-7 illustrate a consistently reduced instrument response for the PE spike mixture compared to the single salt spikes solutions.

The previous PE study discovered that the Arizona and Washington sites were not using the most recent version of calculation software available. This discovery was determined by recalculating raw data provided by each site using a recent version of the Sunset software. In response to the discovery, Sunset installed new versions of the calculation software at the Arizona and Washington sites. Raw data from all sites were again recalculated at NAREL for this study. The recalculated results from Phoenix and Seattle were slightly different from the reported values, indicating a slight difference in software versions still exists. However, the new software installations have significantly reduced the differences between reported and recalculated results at these sites and the Sunset carbon analyzer continues to demonstrate good accuracy and precision performance in the analysis of PE samples at all three field sites.

Table 3. Evaluation of the 8400N Pulse Analyzer								
Site	**Audit Date**	**Audit Time**	***** Span Gas Conc. (ppb)**	**Steady State Check (ppb)**	**Flow Balance Check (ppb)**	**Line Purge (ppb)**	**NOx Pulse Read (ppb*s)**	**Age of Flash Strip (days)**
Arizona	27-Jun-05	4:45 PM	4910	4905.7	4098.2	5.0	3364.3	10
Illinois	09-Jun-05	8:30 AM	5270	5253.6	4600	0.3	3290.8	1
Indiana	28-Jul-05	8:05 AM	5100	5093.1	4494.2	-1.4	2458.4	29
Texas	10-Jun-05	12:03 PM	5593	5606	4752	0.0	2342	3
Washington	13-Jul-05	0845 PST	4860	4861.8	4296.1	0.5	2732.1	8
*** Span gas concentration as labeled on the bottle (should be 5000 ppb).								

Table 4. Aqueous Nitrate Standards								
Site	**Sample ID**	**Volume Deposited (µL)**	**Mass Deposited (ng)**	**Baseline (ppb*s)**	**Corrected Pulse (ppb*s)**	**Measured Mass (ng)**	**Analyzer Flow (L/min)**	**Re-calculated Mass*** (ng)**
Arizona	Local blank water	0.5	0	119.0	57.6	1.9	0.80	6.3
Arizona	Local blank water	0.5	0	129.6	49.3	1.7	0.80	6.0
Arizona	Local blank water	0.5	0	125.7	40.6	1.4	0.80	5.5

Table 4. Aqueous Nitrate Standards								
Site	**Sample ID**	**Volume Deposited (µL)**	**Mass Deposited (ng)**	**Baseline (ppb*s)**	**Corrected Pulse (ppb*s)**	**Measured Mass (ng)**	**Analyzer Flow (L/min)**	**Re-calculated Mass*** (ng)**
Arizona	Local 100 ng/µL std	0.5	50	108.7	1472.0	49.6	0.80	77.0
Arizona	Local 100ng/µL std	0.5	50	109.4	1425.3	48.0	0.80	74.6
Arizona	Local 100ng/µL std	0.5	50	110.1	1427.3	48.1	0.80	74.8
Arizona	N1-05-05	0.5	20	102.0	527.8	17.8	0.80	29.8
Arizona	N1-05-05	0.5	20	107.9	488.8	16.5	0.80	27.9
Arizona	N1-05-05	0.5	20	109.9	553.3	18.7	0.80	31.2
Arizona	N2-05-05	0.5	100	101.8	2238.4	75.4	0.80	115.2
Arizona	N2-05-05	0.5	100	99.4	2350.9	79.2	0.80	120.9
Arizona	N2-05-05	0.5	100	112.2	2377.8	80.1	0.80	122.2
Arizona	N3-05-05	0.5	200	102.6	2609.2	87.9	0.80	133.7
Arizona	N3-05-05	0.5	200	104.4	3004.3	101.2	0.80	153.5
Arizona	N3-05-05	0.5	200	108.6	2658.8	89.5	0.80	136.1
Arizona	N4-05-05	0.5	300	103.8	6550.3	220.6	0.80	330.4
Arizona	N4-05-05	0.5	300	89.2	6495.3	218.8	0.80	327.8
Arizona	N4-05-05	0.5	300	87.0	6149.6	207.1	0.80	310.4
Arizona	N3-05-05	0.5	400	93.2	7585.4	255.5	0.80	382.2
Arizona	N3-05-05	0.5	400	81.2	8195.0	276.0	0.80	412.5
Arizona	N3-05-05	0.5	400	72.2	8468.4	285.2	0.80	426.2
Illinois	Local blank water	0.5	0	-8.0	87.4	3.1	0.84	-4.4
Illinois	Local blank water	0.5	0	-8.4	88.8	3.2	0.84	-4.2
Illinois	Local blank water	0.5	0	-9.7	86.2	3.1	0.84	-4.4
Illinois	Local 100ng/µL std	0.5	50	-12.8	1450.4	51.7	0.84	71.3
Illinois	Local 100ng/µL std	0.5	50	-9.2	1417.9	50.5	0.84	69.5
Illinois	Local 100ng/µL std	0.5	50	-16.7	1359.1	48.5	0.84	66.3

Table 4. Aqueous Nitrate Standards								
Site	**Sample ID**	**Volume Deposited (µL)**	**Mass Deposited (ng)**	**Baseline (ppb*s)**	**Corrected Pulse (ppb*s)**	**Measured Mass (ng)**	**Analyzer Flow (L/min)**	**Re-calculated Mass*** (ng)**
Illinois	N1-05-05	0.5	20	-10.6	572.3	20.4	0.84	22.6
Illinois	N1-05-05	0.5	20	-14.2	598.2	21.3	0.84	24.0
Illinois	N1-05-05	0.5	20	-17.3	609.3	21.7	0.84	24.6
Illinois	N2-05-05	0.5	100	-12.9	2295.0	81.8	0.84	118.2
Illinois	N2-05-05	0.5	100	-13.2	2354.5	83.9	0.84	121.5
Illinois	N2-05-05	0.5	100	-19.6	2310.4	82.4	0.84	119.1
Illinois	N3-05-05	0.5	200	-13.5	2913.2	103.9	0.84	152.6
Illinois	N3-05-05	0.5	200	-14.2	2950.4	105.2	0.84	154.6
Illinois	N3-05-05	0.5	200	-15.0	2907.9	103.7	0.84	152.3
Illinois	N4-05-05	0.5	300	-11.8	6038.2	215.3	0.84	326.1
Illinois	N4-05-05	0.5	300	-11.1	5841.7	208.3	0.84	315.2
Illinois	N4-05-05	0.5	300	-16.5	5945.3	211.9	0.84	320.8
Illinois	N5-05-05	0.5	400	-13.4	7491.7	267.1	0.84	406.8
Illinois	N5-05-05	0.5	400	-13.2	7232.3	257.8	0.84	392.3
Illinois	N5-05-05	0.5	400	-11.2	7536.2	268.7	0.84	409.3
Indiana	Local blank water	0.5	0	-0.7	46.6	1.7	0.84	13.3
Indiana	Local blank water	0.5	0	34.5	37.0	1.3	0.84	12.8
Indiana	Local blank water	0.5	0	23.2	23.3	0.8	0.84	12.2
Indiana	Local 100ng/µL std	0.5	50	-15.1	1509.2	53.6	0.84	77.8
Indiana	Local 100ng/µL std	0.5	50	12.5	1535.5	54.6	0.84	79.0
Indiana	Local 100ng/µL std	0.5	50	-7.1	1482.9	52.7	0.84	76.7
Indiana	N1-05-05	0.5	20	16.4	487.8	17.3	0.84	32.7
Indiana	N1-05-05	0.5	20	-14.6	523.6	18.6	0.84	34.3
Indiana	N1-05-05	0.5	20	7.2	595.5	21.2	0.84	37.6

Table 4. Aqueous Nitrate Standards								
Site	**Sample ID**	**Volume Deposited (µL)**	**Mass Deposited (ng)**	**Baseline (ppb*s)**	**Corrected Pulse (ppb*s)**	**Measured Mass (ng)**	**Analyzer Flow (L/min)**	**Re-calculated Mass*** (ng)**
Indiana	N2-05-05	0.5	100	-6.6	2631.1	93.5	0.84	127.4
Indiana	N2-05-05	0.5	100	9.7	2684.5	95.4	0.84	129.7
Indiana	N2-05-05	0.5	100	-3.0	2628.9	93.4	0.84	127.3
Indiana	N3-05-05	0.5	200	13.4	2680.6	95.3	0.84	129.6
Indiana	N3-05-05	0.5	200	-15.8	2428.9	86.3	0.84	118.4
Indiana	N3-05-05	0.5	200	-3.0	2134.7	75.9	0.84	105.5
Indiana	N4-05-05	0.5	300	-21.7	6974.0	247.9	0.84	319.2
Indiana	N4-05-05	0.5	300	-5.7	7003.8	248.9	0.84	320.4
Indiana	N4-05-05	0.5	300	-52.6	7235.4	257.2	0.84	330.8
Indiana	N5-05-05	0.5	400	-9.9	9451.3	335.9	0.84	428.5
Indiana	N5-05-05	0.5	400	-1.0	9256.0	329.0	0.84	420.0
Indiana	N5-05-05	0.5	400	-7.0	8773.4	311.8	0.84	398.6
Texas	Local blank water	0.5	0	-1.9	70.3	2.7	0.91	3.2
Texas	Local blank water	0.5	0	1.1	43.3	1.1	0.91	1.2
Texas	Local blank water	0.5	0	0.0	34.7	1.3	0.91	1.4
Texas	Local 100ng/µL std	0.5	50	-5.0	1379.4	53.1	0.91	66.9
Texas	Local 100ng/µL std	0.5	50	-2.5	1341.1	51.6	0.91	65.0
Texas	Local 100ng/µL std	0.5	50	-1.9	1261.6	48.5	0.91	61.1
Texas	N1-05-05	0.5	20	-3.2	547.6	21.1	0.91	26.5
Texas	N1-05-05	0.5	20	0.4	519.8	20.0	0.91	25.1
Texas	N1-05-05	0.5	20	-0.2	541.3	20.8	0.91	26.1
Texas	N2-05-05	0.5	100	-1.0	2461.5	94.7	0.91	119.5
Texas	N2-05-05	0.5	100	-2.9	2260.5	87.0	0.91	109.8
Texas	N2-05-05	0.5	100	-10.6	2188.3	84.2	0.91	106.2

Table 4. Aqueous Nitrate Standards								
Site	**Sample ID**	**Volume Deposited (µL)**	**Mass Deposited (ng)**	**Baseline (ppb*s)**	**Corrected Pulse (ppb*s)**	**Measured Mass (ng)**	**Analyzer Flow (L/min)**	**Re-calculated Mass*** (ng)**
Texas	N3-05-05	0.5	200	-5.5	3847.7	148.1	0.91	187.0
Texas	N3-05-05	0.5	200	-3.6	3107.5	119.6	0.91	151.0
Texas	N3-05-05	0.5	200	-1.2	3127.5	120.3	0.91	151.9
Texas	N4-05-05	0.5	300	-2.1	7255.2	279.2	0.91	352.8
Texas	N4-05-05	0.5	300	-2.0	6205.4	238.8	0.91	301.7
Texas	N4-05-05	0.5	300	-4.8	6008.0	231.2	0.91	292.1
Texas	N5-05-05	0.5	400	0.0	8135.8	313.1	0.91	395.6
Texas	N5-05-05	0.5	400	-3.6	8420.5	324.0	0.91	409.4
Texas	N5-05-05	0.5	400	-4.6	8334.7	320.7	0.91	405.3
Washington	Local blank water	0.5	0	2	92.4	3.5	0.89	7.8
Washington	Local blank water	0.5	0	-12.4	40.7	1.5	0.89	5.0
Washington	Local blank water	0.5	0	-17	34.4	1.3	0.89	4.7
Washington	Local 100ng/µL std	0.5	50	-5.1	1422.1	53.7	0.89	76.5
Washington	Local 100ng/µL std	0.5	50	-5.8	1319.9	49.8	0.89	71.2
Washington	Local 100ng/µL std	0.5	50	-10.9	1279.4	48.3	0.89	69.1
Washington	N1-05-05	0.5	20	-11.6	569	21.5	0.89	32.4
Washington	N1-05-05	0.5	20	-4.7	500	18.9	0.89	28.9
Washington	N1-05-05	0.5	20	-12.9	497	18.8	0.89	28.7
Washington	N2-05-05	0.5	100	-6.8	2392	90.3	0.89	126.7
Washington	N2-05-05	0.5	100	-5.1	2172.9	82	0.89	115.3
Washington	N2-05-05	0.5	100	-1.2	2399.8	90.6	0.89	127.1
Washington	N3-05-05	0.5	200	-4.9	2754.1	104	0.89	145.4
Washington	N3-05-05	0.5	200	-15.6	2516.2	95	0.89	133.1
Washington	N3-05-05	0.5	200	-3	2289.8	86.4	0.89	121.3

Table 4. Aqueous Nitrate Standards

Site	Sample ID	Volume Deposited (µL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Washington	N4-05-05	0.5	300	-3.5	6385.1	241	0.89	333.1
Washington	N4-05-05	0.5	300	-8.6	5779.8	218	0.89	301.6
Washington	N4-05-05	0.5	300	-0.7	6603.3	249.3	0.89	344.5
Washington	N5-05-05	0.5	400	-8	7628.8	288	0.89	397.5
Washington	N5-05-05	0.5	400	-4.5	7884.5	297.6	0.89	410.6
Washington	N5-05-05	0.5	400	-7.6	7944.8	299.9	0.89	413.8

****** Results from each site were re-calculated from a calibration curve based upon the PE solutions analyzed at that site.***

Table 5. Evaluation of the 8400S Pulse Analyzer

Site	Audit Date	Audit Time	*** Span Gas Conc. (ppb)	Steady State Check (ppb)	Flow Balance Check (ppb)	Line Purge (ppb)	Age of Flash Strip (days)
Arizona	-----	-----	-----	-----	-----	-----	-----
Indiana	-----	-----	-----	-----	-----	-----	-----
Illinois	08-Jun-05	11:00 AM	750	752	650.8	-0.9	7
Texas	10-Jun-05	12:02 PM	1007	948.3	836.8	0.2	3
Washington	21-Jul-05	1332PST	990	997.1	871.1	-0.3	4
*** *Span gas concentration as labeled on the bottle (should be 1000 ppb).*							

Table 6. Aqueous Sulfate Standards

Site	Sample ID	Volume Deposited (µL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Illinois	Local blank water	0.5	0	-48.0	34.1	2.5	1.08	4.9
Illinois	Local blank water	0.5	0	-63.6	19.3	1.4	1.08	2.8
Illinois	Local blank water	0.5	0	-34.3	21.2	1.5	1.08	3.0
Illinois	Local 300ng/µL std	0.5	150	-53.8	1036.7	73.2	1.08	145.0
Illinois	Local 300ng/µL std	0.5	150	-55.1	1053.7	74.4	1.08	147.3
Illinois	Local 300ng/µL std	0.5	150	-47.0	975.4	68.9	1.08	136.4

Table 6. Aqueous Sulfate Standards								
Site	**Sample ID**	**Volume Deposited (µL)**	**Mass Deposited (ng)**	**Baseline (ppb*s)**	**Corrected Pulse (ppb*s)**	**Measured Mass (ng)**	**Analyzer Flow (L/min)**	**Re-calculated Mass*** (ng)**
Illinois	S1-05-05	0.5	60	-30.4	392.2	27.7	1.08	54.8
Illinois	S1-05-05	0.5	60	-44.8	397.3	28.1	1.08	55.6
Illinois	S1-05-05	0.5	60	-50.0	424.4	30.0	1.08	59.4
Illinois	S2-05-05	0.5	240	-57.0	1668.4	117.8	1.08	233.3
Illinois	S2-05-05	0.5	240	-71.0	1729.5	123.3	1.08	244.2
Illinois	S2-05-05	0.5	240	-37.7	1698.8	119.9	1.08	237.5
Illinois	S3-05-05	0.5	600	-46.2	4281.0	302.2	1.08	598.5
Illinois	S3-05-05	0.5	600	-64.4	4403.8	313.9	1.08	621.7
Illinois	S3-05-05	0.5	600	-92.6	4312.4	307.4	1.08	608.8
Illinois	S4-05-05	0.5	900	-92.6	6418.0	459.5	1.08	910.1
Illinois	S4-05-05	0.5	900	-88.1	6301.4	449.1	1.08	889.5
Illinois	S4-05-05	0.5	900	-88.4	6353.9	452.9	1.08	897.0
Illinois	S5-05-05	0.5	1200	-75.1	8453.2	602.5	1.08	1193.3
Illinois	S5-05-05	0.5	1200	-57.4	8408.0	593.6	1.08	1175.7
Illinois	S5-05-05	0.5	1200	-34.2	8729.9	616.3	1.08	1220.6
Texas	Local blank water	0.5	0	-3.5	8.1	0.8	1.48	30.4
Texas	Local blank water	0.5	0	-4.0	-17.2	-1.7	1.48	26.4
Texas	Local blank water	0.5	0	-15.0	3.7	0.4	1.48	29.7
Texas	Local 300ng/µL std	0.5	150	-34.5	732.5	70.7	1.48	141.7
Texas	Local 300ng/µL std	0.5	150	-5.0	678.1	65.5	1.48	133.4
Texas	Local 300ng/µL std	0.5	150	-25.2	779.6	75.3	1.48	149.0
Texas	S1-05-05	0.5	60	-36.7	256.1	24.7	1.48	68.4
Texas	S1-05-05	0.5	60	-13.8	198.2	19.1	1.48	59.5
Texas	S1-05-05	0.5	60	-24.8	244.3	23.6	1.48	66.7

Table 6. Aqueous Sulfate Standards

Site	Sample ID	Volume Deposited (µL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Texas	S2-05-05	0.5	240	-10.0	1186.6	114.6	1.48	211.6
Texas	S2-05-05	0.5	240	-32.5	1090.2	105.3	1.48	196.8
Texas	S2-05-05	0.5	240	-0.3	1291.3	124.3	1.48	227.1
Texas	S3-05-05	0.5	600	-14.4	3750.5	362.2	1.48	606.0
Texas	S3-05-05	0.5	600	-20.4	3773.8	364.4	1.48	609.5
Texas	S3-05-05	0.5	600	-25.3	4055.9	391.7	1.48	653.0
Texas	S4-05-05	0.5	900	-9.4	5764.3	556.7	1.48	915.8
Texas	S4-05-05	0.5	900	-24.0	5934.2	573.1	1.48	941.9
Texas	S4-05-05	0.5	900	-6.0	5794.5	559.6	1.48	920.4
Texas	S5-05-05	0.5	1200	-18.8	7539.0	728.0	1.48	1188.6
Texas	S5-05-05	0.5	1200	-27.7	7562.0	738.9	1.48	1206.0
Texas	S5-05-05	0.5	1200	-37.3	7150.3	690.5	1.48	1128.9
Washington	Local blank water	0.5	0	-54	25.5	2.3	1.39	-5.3
Washington	Local blank water	0.5	0	-52.4	-1.9	-0.2	1.39	-10.2
Washington	Local blank water	0.5	0	-62.8	45.2	4.01	1.39	-2.0
Washington	Local 300ng/µL std	0.5	150	-57.4	746.7	67.9	1.39	122.5
Washington	Local 300ng/µL std	0.5	150	-72.8	574.7	52.3	1.39	92.1
Washington	Local 300ng/µL std	0.5	150	-71.3	706.7	64.3	1.39	115.5
Washington	S1-05-05	0.5	60	-73.6	304.7	27.7	1.39	44.2
Washington	S1-05-05	0.5	60	-73.4	280.4	25.5	1.39	39.9
Washington	S1-05-05	0.5	60	-25	271.3	24.7	1.39	38.3
Washington	S2-05-05	0.5	240	-69.9	1457.1	132.6	1.39	248.5
Washington	S2-05-05	0.5	240	-47.7	1147.8	104.4	1.39	193.6
Washington	S2-05-05	0.5	240	-53.7	1519.2	138.2	1.39	259.4

Table 6. Aqueous Sulfate Standards

Site	Sample ID	Volume Deposited (µL)	Mass Deposited (ng)	Baseline (ppb*s)	Corrected Pulse (ppb*s)	Measured Mass (ng)	Analyzer Flow (L/min)	Re-calculated Mass*** (ng)
Washington	S3-05-05	0.5	600	-55.8	3797.7	345.5	1.39	663.3
Washington	S3-05-05	0.5	600	-72	3565.5	324.4	1.39	622.2
Washington	S3-05-05	0.5	600	-81.8	3611.5	328.6	1.39	630.4
Washington	S4-05-05	0.5	900	-72.6	5273.8	479.8	1.39	925.0
Washington	S4-05-05	0.5	900	-111.2	5579.7	507.7	1.39	979.3
Washington	S4-05-05	0.5	900	-82.6	4803.7	437.1	1.39	841.8
Washington	S5-05-05	0.5	1200	-68	6793.6	618.1	1.39	1194.4
Washington	S5-05-05	0.5	1200	-56.7	6697.6	609.4	1.39	1177.5
Washington	S5-05-05	0.5	1200	-49.2	6498.5	591.3	1.39	1142.2

****** Results from each site were re-calculated from a calibration curve based upon the PE solutions analyzed at that site.***

Table 7. Reported Results														
Sample ID	Sample Description	AZ Results (µg/sample)			IL Results (µg/sample)			WA Results (µg/sample)			NAREL Results - STN Method* (µg/sample)		
		EC	OC	TC	EC	OC	TC	EC	OC	TC	EC	OC	TC
C1	blank filter	0.01	3.44	3.45	0.00	1.55	1.55	0.00	1.68	1.68	0.00	0.70	0.70 +/- 0.64
C1 dup	blank filter	0.01	3.86	3.87	0.00	1.28	1.29	0.00	1.47	1.47	0.00	0.88	0.88 +/- 0.64
C2	35 µgC sucrose spike	0.00	33.85	33.85	0.00	36.18	36.18	0.00	37.64	37.64	0.00	36.68	36.68 +/- 2.13
C2 dup	35 µgC sucrose spike	0.00	34.90	34.90	0.00	36.40	36.40	0.00	37.74	37.74	0.00	34.23	34.23 +/- 2.01
C3	ambient PM2.5	1.91	36.14	38.05	2.70	37.25	39.95	1.73	39.56	41.29	2.94	37.97	40.91 +/- 2.65
C3 dup	ambient PM2.5	3.10	34.25	37.35	2.77	38.02	40.79	1.57	38.29	39.86	3.01	35.20	38.21 +/- 2.51

NAREL results were determined using the filter based method that is approved for the Speciation Trends Network.

Table 8. Recalculated Field Results										
Sample ID	Sample Description	AZ Results (µg/sample)			IL Results (µg/sample)			WA Results (µg/sample)		
		EC	OC	TC	EC	OC	TC	EC	OC	TC
C1	blank filter	0.01	3.25	3.26	0.00	1.55	1.55	0.00	1.80	1.80
C1 dup	blank filter	0.01	3.83	3.84	0.00	1.28	1.29	0.00	1.78	1.78
C2	35 µgC sucrose spike	0.00	33.80	33.80	0.00	36.18	36.18	0.00	37.67	37.67
C2 dup	35 µgC sucrose spike	0.00	34.73	34.73	0.00	36.40	36.40	0.00	37.83	37.83
C3	ambient PM2.5	1.90	38.55	40.45	2.70	37.25	39.95	1.75	39.58	41.33
C3 dup	ambient PM2.5	2.85	35.35	38.20	2.77	38.02	40.79	1.60	38.31	39.92